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ENVIRONMENTAL HYDROCARBON HARVESTING FOR MICRO-SCALE POWER

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Environmental Hydrocarbon Harvesting for Micro-scale Power Sources using Thermopower Waves

Final Performance report: Non DOD Cap Funds – Strano
Grant Number: FA9550-09-1-0700

Executive Summary

Thermopower waves are self-propagating exothermic reaction waves that travel along a thermally conductive nano-conduit such a nanowire or nanotube, inducing a concomitant, high power electrical pulse. Discovered and reported by our lab at MIT in 2010, such waves have already demonstrated specific power density far in excess of conventional Li ion batteries. Our AFOSR sponsored program has explored the theoretical and experimental aspects necessary to use this concept to enable fundamentally new energy harvesting devices. The device design in this project is to scavenge fugitive hydrocarbon emissions from the environment and generate high power pulses to supply energy to remote sensors, communication devices and instrumentation along networks. The previous project period has been highly successful with several key accomplishments:

1) We have developed the theory of excess thermopower describing thermopower waves including the first analytical solution for the entire class of mathematical reaction and thermal diffusion problems (the Zeldovich equations), studied numerically by many for more than 90 years until rendered obsolete by our analysis.
2) We have increased the output voltage and efficiencies of thermopower wave devices from a laboratory curiosity in 2010 (200 mV, 0.001% efficiency) to within range of practical usage (0.01% and rising) in 2013, a 1000-fold increase in efficiency over just 3 years.
3) We have successfully launched thermopower waves with organic fuel vapor (methanol and formic acid) enabling hydrocarbon energy harvesting in a novel pulsed reactor design.
4) We have studied the scaling of thermopower wave devices to gain more insight into modeling their operation as voltage sources.
5) We have successfully demonstrated improving the efficiency of operation by moving towards newer fuels and by harvesting the radiative energy output.

Additionally, our theoretical work on two dimensional (2D) thermopower waves led to an unexpected discovery which we call superadiabaticity, or a process wherein a reflected wave can exceed the adiabatic reaction temperature. This new property holds intriguing possibilities for concentrating energy and ultra-low loss transmission.

Our project produced 8 peer-reviewed publications, including a seminal contribution in Nature Materials, and one US patent. The work in this project also enabled dissertations of four students, two already published and two currently in progress.

Introduction

Thermopower waves is a novel phenomenon discovered in our lab. It is a means of converting chemical energy into electrical energy via self-propagating reaction waves. A thermopower wave device is made by coating a layer of fuel on a thermal conduit. After initiating the chemical reaction at one end of the conduit, the heat of reaction is then carried ahead along the length of the conduit because of its high thermal conductivity. This initiates the fuel lying in its path along the length of the conduit. Thus a thermal and a reaction wave is sustained. Due to the combined effect of difference in temperature and difference in the chemical potential between the reacted and un-reacted region of the fuel, we obtain an electrical output across the two ends of the thermal conduit. On account of the reaction wave, this

phenomenon of thermopower waves gives an electrical power output higher than just expected by thermoelectricity. The peak specific power was found to be as high as 7 kW kg^{-1}. Additionally, an analytical expression governing the temperature of such a reaction wave-front was found in our lab. Effect of functionalization of the thermal conduit used for launching thermopower waves was also studied.

Project Progress to Date (past 5 years)

During the previous project period, we have made tremendous strides from the first demonstration of thermopower waves in carbon nanotubes to further analytical and theoretical understanding of the reaction mechanisms, and expanding into different fuels, different nanotube sources, and new device concepts. Our work has resulted in several well-received articles.

First Demonstration: Chemically Driven Carbon-Nanotube-Guided Thermopower Waves

Theoretical calculations predict that by coupling an exothermic chemical reaction with a nanotube or nanowire possessing a high axial thermal conductivity, a self-propagating reactive wave can be driven along its length. Such waves are realized using a 7-nm cyclotrimethylene trinitramine (TNA) annular shell around a multiwalled carbon nanotube and are amplified by more than 10^4 times the bulk value, propagating faster than 2 m s^{-1}, with an effective thermal conductivity of 1.28±0.2 kW m^{-1} K^{-1} at 2,860 K. This wave produces a concomitant electrical pulse of disproportionately high specific power, as large as 7 kW kg^{-1}, which we identify as a thermopower wave. Thermally excited carriers flow in the direction of the propagating reaction with a specific power that scales inversely with system size. The reaction also evolves an anisotropic pressure wave of high total impulse per mass (300 N s kg^{-1}). Such waves of high power density may find uses as unique energy sources.(1, 2)

In Figure 1 (a), a schematic illustration of the thermopower reaction wave is shown. The experimental setup for measuring voltage pulses generated by the thermopower reaction wave and the dependence of the voltage polarity on reaction direction is shown in Figure 1 (b). The voltage pulses with opposite polarities are shown in Figure 1 (c). In Figure 1 (d), video frames capture the progress of a thermopower reaction wave as it traverses the conduit.

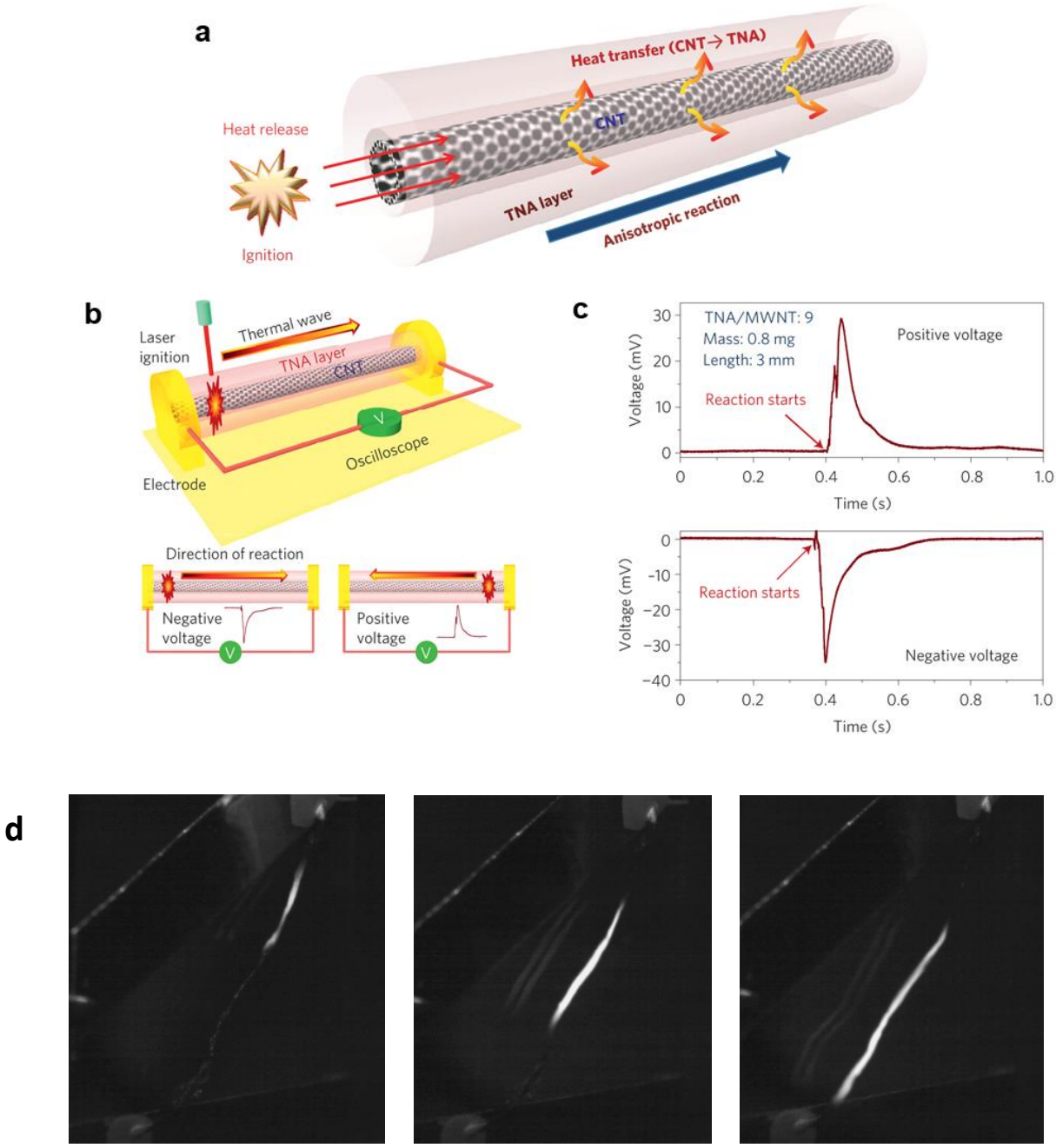

Figure 1: (a) Schematic illustration of thermopower wave reaction. (b) Schematic of measuring voltage generated by thermopower wave, and how direction of reaction changes polarity of voltage pulse. (c) Experimentally measured voltage traces for positive and negative pulses. (Adapted from Ref. (1)) (d) Video frames demonstrating the propagation of a thermopower reaction wave.

Wave front Velocity Oscillations of Carbon-Nanotube-Guided Thermopower Waves: Theory and Experiment

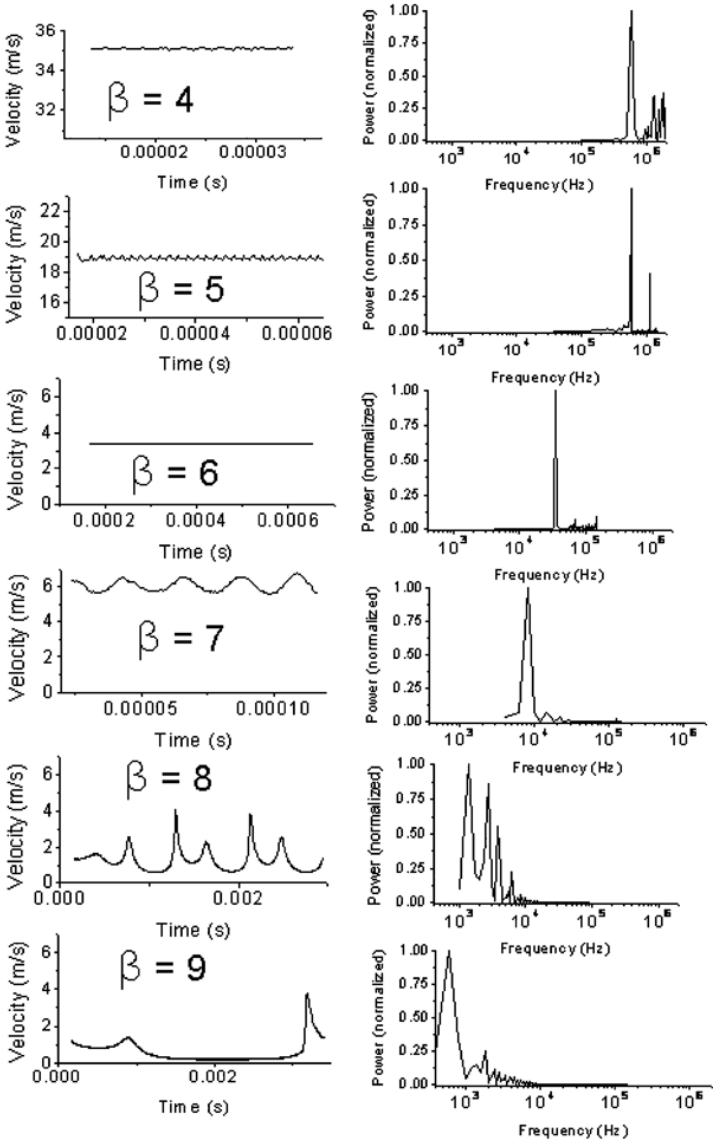

Figure 2: Wave front velocity profiles and frequency spectra for systems with β values from 4 to 9. Oscillations are seen to increase in amplitude and decrease in frequency for increasing β. For β > 7, additional components and complex features are seen. (Adapted from Ref. (3))

We have developed the theory of thermopower waves and analyzed them experimentally, showing that for certain values of the chemical reaction kinetics and thermal parameters, oscillating wave front velocities are possible.(3) Such oscillations were experimentally demonstrated using a cyclotrimethylene-trinitramine / multiwalled carbon nanotube system, which produces frequencies in the range of 400 to 5000 Hz. The propagation velocity oscillations and the frequency dispersion are well described by Fourier's law with an Arrhenius source term accounting for reaction and a linear heat exchange with the nanotube scaffold. The frequencies are in agreement with oscillations in the voltage generated by the reaction. (3) These thermopower oscillations may enable new types of nanoscale power and signal processing sources.

In Figure 2, calculated velocity vs. time profiles are shown for several values of the dimensionless parameter $\beta = (C_p E_a)/(-\Delta H R)$, equivalent to the inverse adiabatic reaction temperature rise.(1, 3) Here, C_p is specific heat, ΔH is the enthalpy of reaction, R is the universal gas constant, and E_a is the activation energy of the reaction. We see thermopower oscillations that increase in amplitude and decrease in frequency with increasing β. In experiments, we are able to observe voltage traces with oscillatory behavior during the reaction phase, but smooth non-oscillatory behavior during the cooling phase.

First Analytical Solution to Coupled Chemical Reaction and Thermally Diffusing Systems

Problems involving chemical reaction coupled to thermal diffusion are central in the chemistry and physics of propulsion, self-propagating high-temperature synthesis (SHS) of materials, and new approaches to power generation involving thermopower waves. We present an analytical solution to a one-dimensional Fourier description of heat propagation in a solid reactant, with a first-order chemical reaction of Arrhenius form providing a thermal source. A generalized logistic function can completely determine the form of the temperature and concentration profiles within the solid, as well as the velocity of the reaction wave under a wide range of conditions. This alternative to the common

asymptotic and three-zone approximate solution methods in the literature requires fewer assumptions and is valid at all time and length scales. The solution is limited to cases where the reaction wave velocity is constant but can be generalized to nth-order kinetics.(4)
The analytical equation for dimensionless temperature, similar to the form of logistic function is

$$u_{ana}(\eta) = \frac{(\frac{1}{\beta})}{(1 + Qe^{cQ\eta})^{1/Q}}$$

Here, η is a combined space and time moving coordinate, c is the wave velocity and β is the non-dimensional inverse adiabatic reaction temperature. The non-dimensional adiabatic temperature rise is the property of the fuel.

Q is a logistic symmetry parameter which was empirically found to be a function of β.

Figure 3 shows the temperature profile from the analytical solution at different values of β compared to numerically computed results.(4)

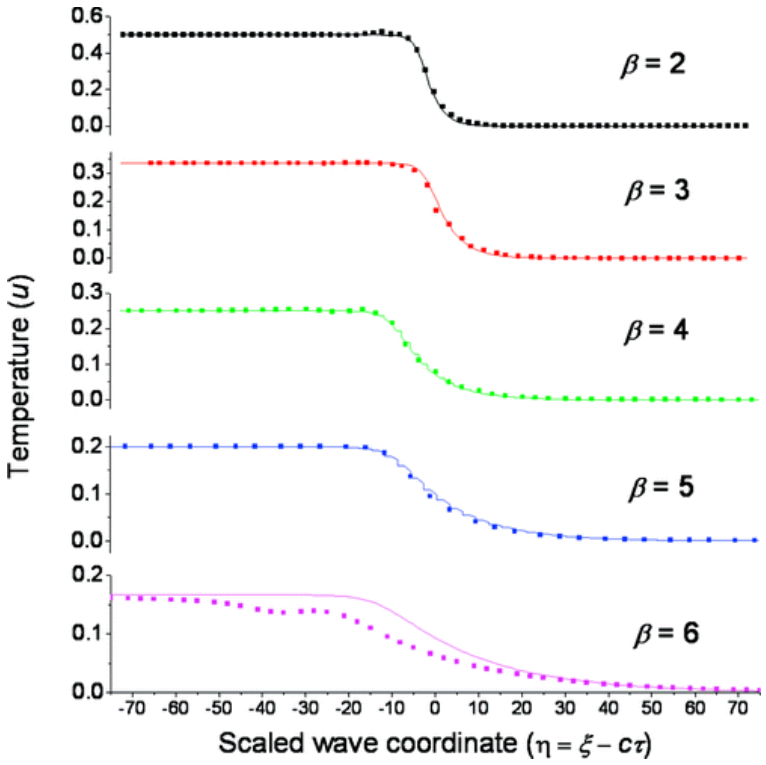

Figure 3: Analytical and numerical solutions using a logistic temperature profile. Analytical solutions are represented by lines, numerical solutions by points. The profiles match closely for several different values of β. Above β = 6, the logistic form becomes less accurate. (Adapted from Ref. (4))

Testing of Alternative Conduits for Thermopower Waves: Nitrobenzene Adducts

We also tried to explore the effects of reactions on nanomaterial conduits to increase their energy density. We exploited diazonium chemistry to synthesize single-walled carbon nanotubes decorated with mono-, di-, and trinitrobenzenes.(5) Figure 4a illustrates the incorporation of trinitrobenzenes along a single-walled carbon nanotube. Data from differential scanning calorimetry showed lower values for activation energy, especially at lower conversion.

The introduction of covalent functionalization reduces electrical and thermal conductivity because of defects that tend to scatter electrons and phonons. However, we were still able to successfully launch thermopower waves and produce electrical power from such functionalized conduits. Results showed that functionalization did not vary the generated electrical power significantly. This work widened the scope of materials that can be successfully used as conduits for thermopower waves. Figure 4b shows the increase in the disorder mode because of covalent functionalization of nanotubes. Figure 4c shows FT-IR results confirming attachment of nitro groups on carbon nanotubes.(5)

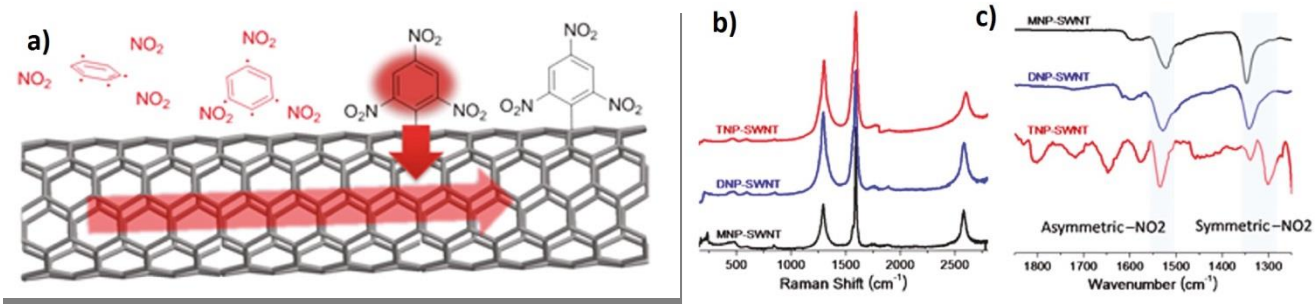

Figure 4: (a) Schematic representation of reaction propagation on a single-walled carbon nanotube decorated with energetic molecules (trinitrobenzenes). (b) Disorder modes increased in Raman spectra after covalent functionalization (c) FT-IR spectra measured on films with ATR (attenuated total reflectance) confirmed presence of nitro groups. MNP-, DNP-, and TNP-SWNTs stand for mono-, di-, and trinitrophenyl-functionalized SWNTs, respectively. (Adapted from Ref. (5))

Theory of Thermopower Waves: Excess Thermopower

Thermopower waves differ from conventional thermopower. In that, thermopower waves rely on good thermal and electrical conductivity of conduits in order to produce a self-propagating reaction wave and generate unipolar voltage across the ends of the conduit. Conventional theories of thermoelectricity and Seebeck coefficient are unable to predict the electrical behavior of thermopower wave devices. We studied the differences in these two phenomena of conventional thermoelectricity and thermopower waves devices to devise a quantitative theory that describes the energetics and electrical dynamics of thermopower waves.(6)

We begin by using drift-diffusion equation used to describe thermoelectric effect.

$$J = -\sigma_h \left(E + \frac{\Delta\mu}{e} \right) - L_{12} \nabla T$$

Here, the electrical conductivity is given by σ_h, electric field by E, chemical potential by μ, elementary charge by e, the Onsager coupling coefficient by L_{12} and the temperature by T. In the limit of zero current density, simplifying for the electric field, we obtain an expression for the potential difference V across the ends of the device, x_R and x_L.

$$V = -\int_{x_L}^{x_R} \frac{\nabla\mu}{e} - \frac{L_{12}}{\sigma_h} \nabla T dx$$

Seebeck coefficient Γ is defined as

$$\Gamma = \frac{L_{12}}{\sigma_h}$$

For conventional thermoelectric measurements which do not include a doping gradient i.e. Δμ=0, the reference Seebeck coefficient Γ_{ref} is used. Thus, the substituted equation for potential difference can be re-written as

$$\therefore V = -\int_{x_L}^{x_R} \frac{d\mu}{e} + \int_{T_L}^{T_R} \Gamma_{ref} dT$$

$$\therefore V = \frac{1}{e}(\mu_L - \mu_R) + \int_{T_L}^{T_R} \Gamma_{ref} dT$$

Thus, the systems exploiting the difference in chemical potential across the electrical contacts will produce higher electrical output than just by the conventional thermoelectric effect. We attribute this changing chemical potential, because of the propagating reaction wave front, to the better-than-thermoelectric performance of thermopower wave devices.

Our thermopower wave devices produce an excess thermopower additive to the static Seebeck prediction. This excess thermopower is defined as:

$$P_{xs} = P_{out} - P_{TE} = \frac{V_{out}^2}{R_c} - \frac{V_{TE}^2}{R_c}$$

Here, P_{TE} corresponds to the conventional thermoelectric prediction whereas P_{out} corresponds to the actual experimental output. The change in chemical potential upon chemical reaction of the fuel has been attributed as the cause of this excess power. This change in chemical potential, because of doping caused by adsorption of fuel, was confirmed by performing Raman analysis of the carbon nanotube conduits. An up-shift in the G^- peak of 5 cm^{-1} was observed during Raman analysis of fueled single walled carbon nanotubes. This is almost equivalent to a doping of 25 holes/µm. This can lead to a chemical potential difference of up to 100 mV between the fueled SWNT region and the un-fueled region behind the wave front. For certain thermopower devices, this increase in thermopower can be as high as 160 % when compared to conventional thermopower. The theory of excess thermopower opens up further avenues to increase the electrical energy output by using conduits with higher Seebeck coefficient and doping conduits appropriately to increase their excess thermopower.[5]

Energy Harvesting from Fugitive Emissions: Thermopower from Adsorbed Liquid Fuels

Current thermopower devices employ solid fuels like nitrocellulose and cyclotrimethylene trinitramine (TNA).(7) The method of manufacturing these devices prevents continuous operation of thermopower power sources because the fuels are not easily refueled and are completely consumed in the reaction. Hence, taking this concept forward to make it into a continuous electricity generation device, we are now working on developing what we call a 'fuel cell' which uses the concept of thermopower waves being applied to liquid fuels. Taking advantage of exothermic combustion reaction of liquids like formic acid, methanol, ethanol etc., will prove beneficial in exploiting the liquid chemical energy along with the excess thermopower as caused by change in chemical potential after the reaction. Using liquid fuels would involve doping the conduit with appropriate catalyst to reduce the energy of activation of the combustion reaction. As with the case of conventional thermopower devices, experiments were tried with carbon nanotubes doped with catalysts like platinum (Pt) nanoparticles, Pt supported on alumina, etc. Experiments were carried out using liquid formic acid as the fuel and a butane torch as the source of ignition. Successful voltage output was obtained from such devices, with the efficiencies comparable to that of the previous solid fuel devices. Moreover, these results were reproducible even when using the same conduit multiple times in a repeated operation, a necessary step before realizing continuous operation. However, further investigation of this 'fuel cell' setup revealed that the increase in temperature and observed Seebeck effect arose because of H_2 combustion rather than fuel combustion. Analysis showed that most of the liquid fuel evaporated because of initiation input heat. So the fuel cell setup was modified to exploit vapor phase fuel reaction. Figure 5 shows a schematic of the vapor phase fuel cell setup, as well as a photograph of the actual device. Preliminary work was carried out to confirm fuel combustion in vapor state and the presence of temperature spikes corresponding to the exothermic nature of the reaction. A sample temperature profile for reaction of methanol over catalysts of Pt

nanoparticles and Pt on carbon is shown in the figure below. Work is now in progress to record voltage output from the fuel cell setup based on a vapor phase flow of fuels like methanol or formic acid. Figure 5 shows the experimental temperature data obtained when reacting vaporized methanol using Pt on carbon and Pt nanoparticles alone, which will be attached to carbon nanotube conduits in our future work.

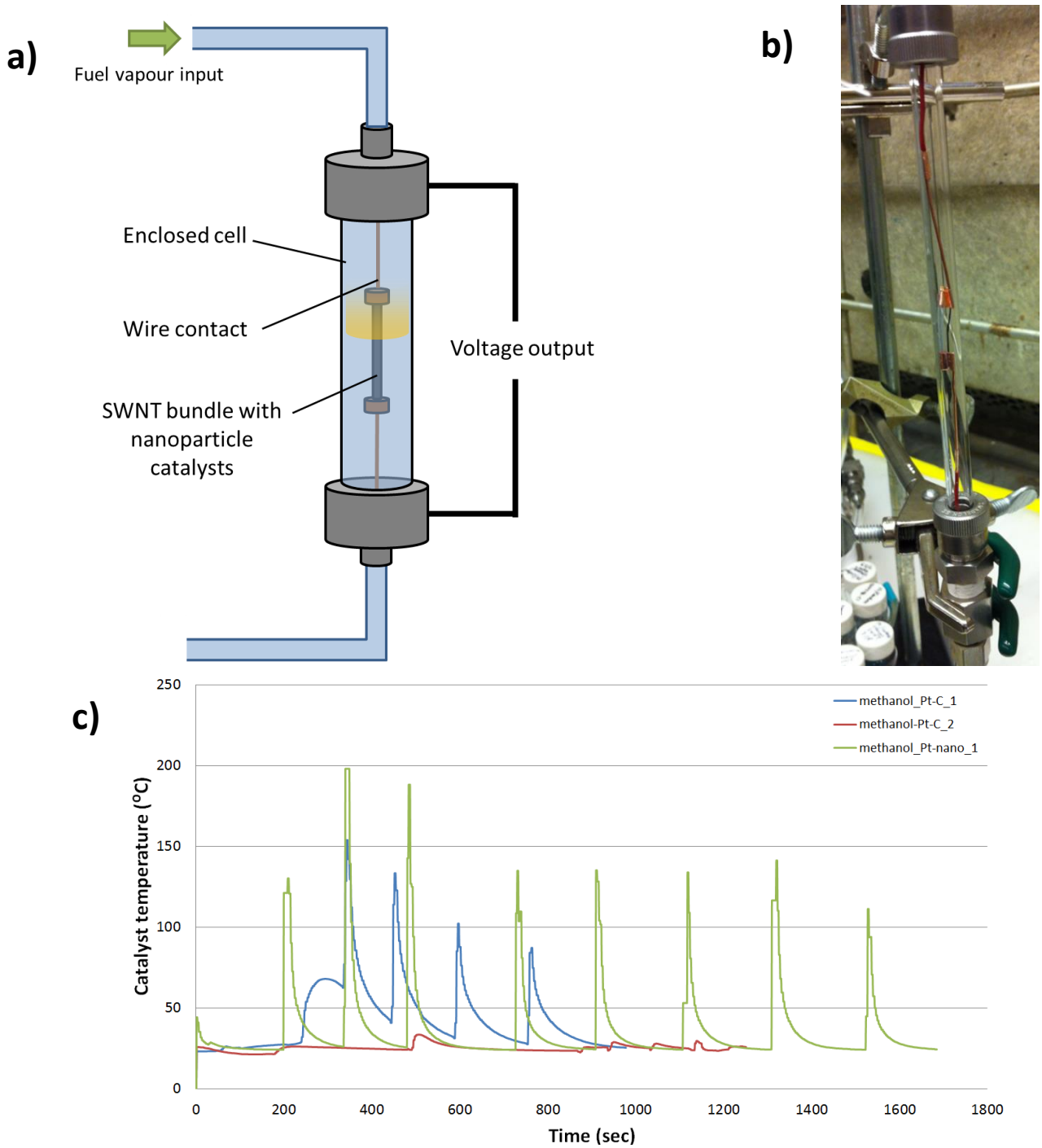

Figure 5: (a) Schematic of thermopower wave fuel cell. (b) Photograph of thermopower wave fuel cell implementation: quartz reactor tube with single walled carbon nanotube (SWNT) yarn bundle inside. For temperature data collection, one end of the quartz tube was filled with a cluster of catalyst particles where the exothermic reaction occurs. (c) Temperature plots showing spikes in temperature corresponding exothermic methanol reaction on catalysts Pt supported on carbon and Pt nanoparticles

Scalability of 1D Thermopower Waves and Electrical Representation of Thermopower Wave Devices

To study the scalability of thermopower wave systems, we carried out an analysis by launching reaction waves on thermal conduits of varying lengths, l_{exp}. Single walled carbon nanotubes coated with nitrocellulose and sodium azide were used for this study. Both the open circuit voltage data, V_{OC} and voltage data across an external resistance, V_{out} were collected. In order to maximize the power extracted from the circuit, we carried out impedance matching such that the external circuit resistance was chosen to be around the device's resistance before launching the reaction. To better study the effect of the increase in the propagation length of the reaction wave, i.e. l_{prop}, on properties such as the voltage peak, we decided to study the time-averaged voltage. To evaluate it, we considered the total duration for non-zero voltage output, Δt, and used it with the area under the voltage curve to obtain a representative time-averaged voltage. Thus the average output voltage is given by

$$\overline{V_{out}} = \frac{\int_{t=0}^{t=t_{end}} V_{out} dt}{\Delta t}$$

We hypothesized two possible outcomes of readings for different l_{prop}. With increasing l_{prop}, either the amplitude of the maximum voltage might increase because of any possible changes in the chemical potential gradient or the duration of the voltage output might increase because of the gradients (both temperature and chemical potential) being sustained for longer time as the reaction wave theoretically propagates at a constant velocity. Our analysis showed the latter to be true.

Our next step was to study the voltage output as a function of the device. Two distinctive properties, the device internal resistance and the length of the thermal conduit were considered.
As with electrical conductors, the internal resistance of the device, mainly contributed to by the carbon nanotubes was assumed to be a function of its length. Thus, the system could then be modeled as a galvanic cell having an internal resistance contributed to by the electrical resistance of the carbon nanotubes, R_{int} and an external resistance, R_{ext} with current, i in the circuit.

$$\overline{V_{out}} = \overline{V_{OC}} - iR_{\text{int}}$$
$$\therefore \overline{V_{out}} = \overline{V_{OC}} - i(R_{\text{int},0}L_{\exp})$$
$$\therefore \overline{V_{out}} = \overline{V_{OC}} - \left(\frac{\overline{V_{out}}}{R_{ext}}\right)(R_{\text{int},0}L_{\exp})$$
$$\therefore \overline{V_{OC}} = \overline{V_{out}}\left(1 + \frac{R_{\text{int},0}L_{\exp}}{R_{ext}}\right)$$

This equation was then used to analyze our experimental data. For all the thermopower reaction waves launched with impedance matched external resistance, the average output voltage $\overline{V_{out}}$ was calculated. Then, using the device internal resistance at the start of the reaction ie. $R_{\text{int},0}L_{\exp} \sim R_{\text{int}}(t=0)$, we calculated the average open circuit voltage corresponding to each device $\overline{V_{OC}}$. For a perfect power source, we expect the open circuit voltage to stay constant. However, for the samples we have recorded so far, we obtain a range of values for the predicted averaged open circuit voltage. The histogram in Figure 6 c below shows this data (voltage in mV).

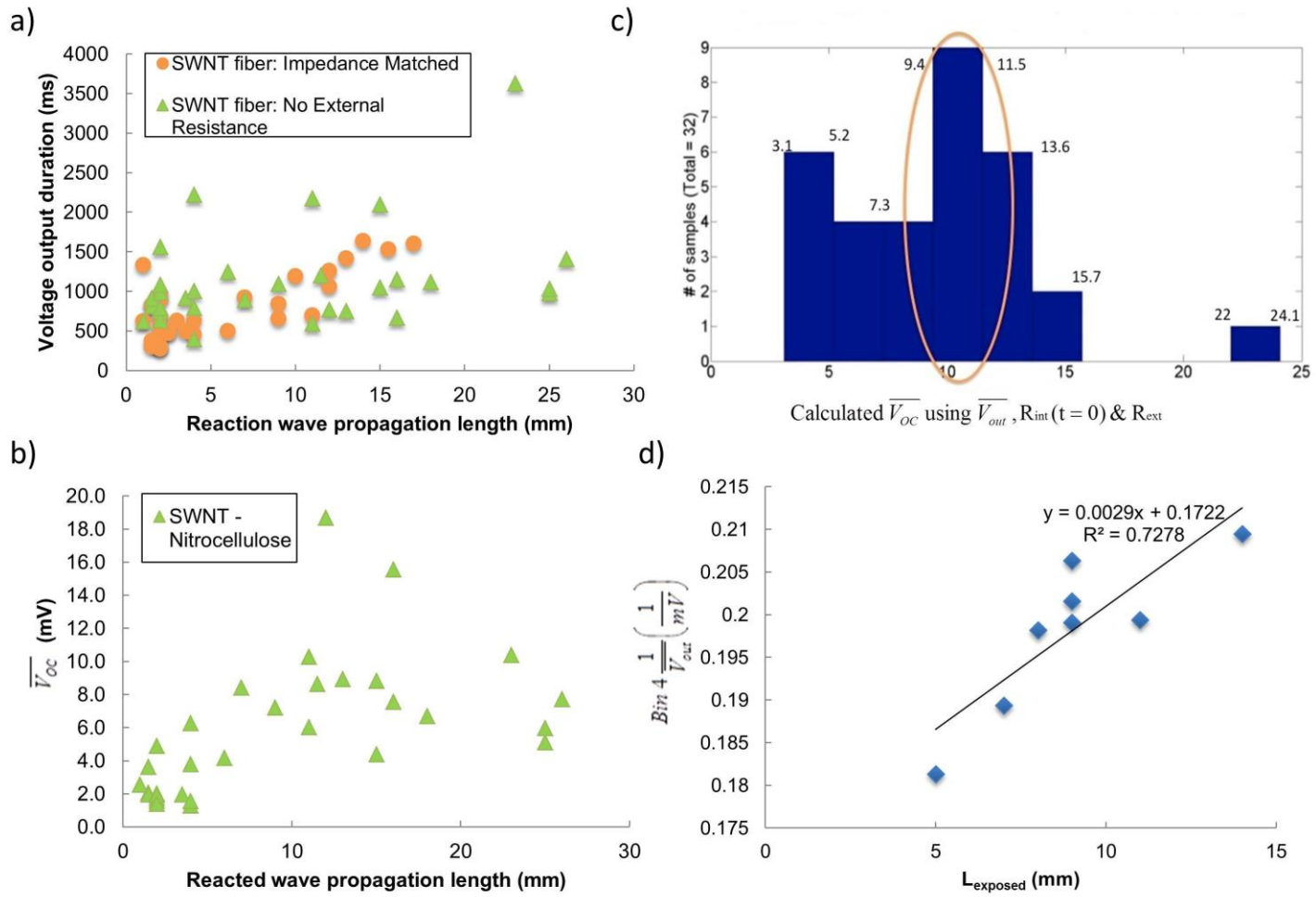

Figure 6: (a) Plot of the duration of voltage output versus the length of the reaction wave. This duration includes the time of reaction as well as the cooling time reflected by the time period corresponding to reducing voltage output. We see an increase in the duration which is expected since theoretically, the reaction wave travels at a constant velocity for any given fuel-thermal conduit system (b) Experimentally obtained time-averaged open circuit voltage, $\overline{V_{OC}}$ is plotted against the length of the corresponding reaction wave. (c) This histogram is plotted for values of calculated $\overline{V_{OC}}$ as obtained using experimental data for impedance matching experiments on SWNT – Nitrocellulose thermopower wave systems. The plot shows that the current fuel-thermal conduit system shows a dominant $\overline{V_{OC}}$. (d) The experimental data corresponding to the 4th bin in histogram shown in part (c) is analyzed as a voltage source.

To further study the operation of the thermopower wave devices, we decided to focus on the experimental data corresponding to the mode of $\overline{V_{OC}}$, as show in the histogram. We rearranged the above master equation to obtain a linear relationship between the averaged voltage output and the exposed length of the device.

The equation we studied is

$$\overline{V_{OC}} = \overline{V_{out}}\left(1 + \frac{R_{\text{int},0} L_{\text{exp}}}{R_{ext}}\right)$$

$$\therefore \frac{1}{\overline{V_{out}}} = \frac{1}{\overline{V_{OC}}} + \frac{1}{\overline{V_{OC}}} \frac{R_{\text{int},0}}{R_{ext}} L_{\text{exp}}$$

The analysis for the mode of the histogram shows a linear relation with a regression coefficient of about 0.72 for a relation between $\frac{1}{\overline{V_{out}}}$ and L_{exp}. Including R_{ext} in the analysis as a parameter in x-axis component leads to a reduction in the fit. To study this further, experiments will be carried where the same exercise will be repeated for multiple reaction waves launched for a constant external circuit resistance. With the current analysis, an averaged open circuit voltage value is also outputted by the regression fit. This value matches well with the average value of the corresponding bin of the histogram. This shows galvanic cell performance by thermopower wave devices which have similar open circuit voltage. Further work in this field will be dedicated to collecting more data to test this observation. Efforts will be dedicated to study the factors that could be possibly leading to different open circuit voltage output within devices made of the same set of fuel-thermal conduit. This will not only lead to improved understanding about thermopower waves but will also allow us to predict its use in applications needing longer reaction waves to be launched.

Alternative Fuels to Improve the Efficiency of Operation of Thermopower Wave Devices

Theory of excess thermopower predicts the fuel to play a very important role in a thermopower wave device's operation. The voltage output attributed to the thermoelectricity of the thermal conduit depends on the temperature gradient established during the reaction propagation, which in turn is governed by the fuel properties. Similarly, the effect of doping by the fuel molecules adsorbed atop the thermal conduit impacts the excess thermopower output. Thus the fuel chosen plays a very dominant role in the operation of a thermopower wave device. Previous work in the field of thermopower waves has been carried out with high energy content fuels such as nitrocellulose, picramide etc. With the long-term aim of making portable fuel sources using thermopower wave technology, we want to test fuels that have lower energy content and that are safe to handle.

With this in mind, we decided to extend this operation to more easily accessible fuels such as sucrose and less energy-dense fuel such as sodium azide. Thermopower waves were launched by coating sodium azide (which was used as an initiator in one of the previous fuel mixtures) on single walled carbon nanotubes. Tests were also carried out for fuel of mixtures of sucrose and potassium nitrate (mass ratio of 7:13). We were able to successfully launch thermopower waves for both these fuels. As seen in Figure 7, devices using sodium azide showed the highest efficiency, reaching about 0.1%, compared to 0.001% shown by sucrose-KNO_3 devices and 0.0001% shown by traditional nitrocellulose-sodium azide devices. Thus, fuels play an important role in the operation of thermopower wave devices. Future work will focus on studying the factors contributing to higher efficiency of some fuels and extend this knowledge to increase the library of possible fuels that can be used to launch high efficiency thermopower waves.

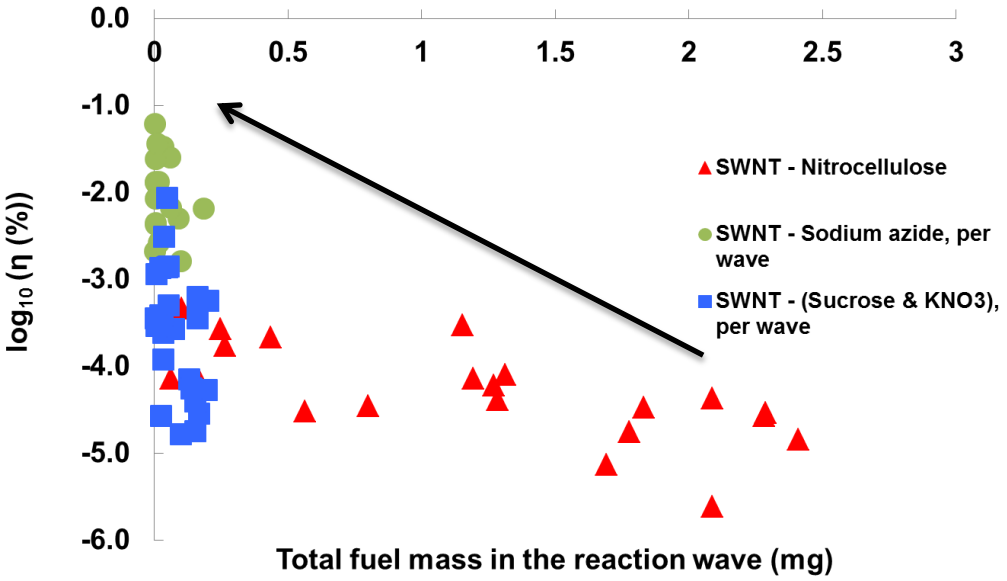

Figure 7: Efficiency of thermopower wave devices for different fuels. As seen from the log plot above, in terms of chemical to electrical conversion efficiency, sodium azide performed better than the fuel mixture of sucrose and potassium nitrate, which, in turn, was better than the traditional nitrocellulose (with sodium azide initiator)

Alternative Device Configuration to Improve the Efficiency of Operation of Thermopower Wave Devices by Harvesting Heat Losses

We performed preliminary experiments using thermoelectrics to harvest the radiative energy given out by fuel reaction. By keeping thermoelectric energy harvesters in the proximity of a propagating reaction wave, we thermalize the radiation energy emitted by the propagating reaction front. Thus, we increase the percentage of the amount of energy that is given out by the chemical reaction that is effectively converted into electrical energy.

Accordingly, first the experimental design was modified with a Bi_2Te_3 thermoelectric (TE) energy harvester on top of a thermopower wave device using the nitrocellulose fuel mixture. Since we want to study harvesting of just the energy given out the reaction and not the input energy used to initiate the reaction, we made sure that the TE harvester was not exposed to the heat radiated by the input heat in the form of joule heater brought in contact with one of the ends of the thermopower device. Our preliminary experiments showed a distance of about 4mm between the point of thermopower wave initiation and the suspended joule heater being enough to isolate the effect of input heat and the heat of reaction. For samples where long enough reaction waves were launched, we were successfully able to obtain an electrical output not only from the thermopower wave device but also the thermoelectric atop it.

After this, thermopower waves were launched for suspended devices where the fuel coated carbon nanotube was contacted with just the copper tape electrodes. TE harvesters were placed both above and below this device to improve the net efficiency for electrical energy that can be extracted from the system. As can be seen in Figure 8, this improved design increased the average efficiency of operation to previously unreported values in excess of 1%.

This brings forth more opportunities that can be explored to improve efficiency. Having the thermopower device suspended (instead of being placed on a glass slide) can allow us to harvest the radiative energy given out by the propagating reaction wave-front from all directions. This experimental design can be combined with higher efficiency fuels such as sucrose and sodium azide to improve the net efficiency of operation.

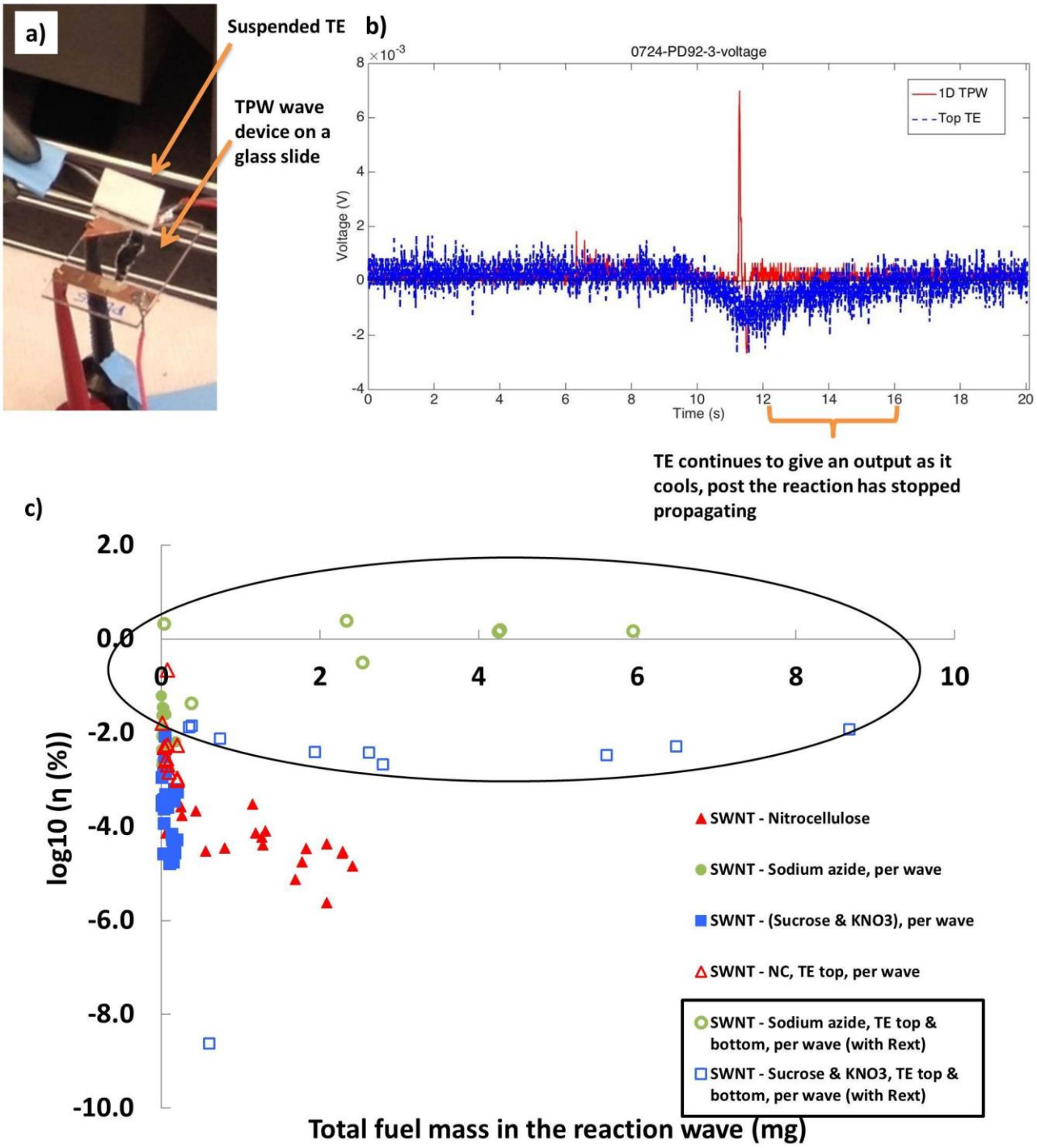

Figure 8: a) A photograph of the experimental setup consisting of the traditional thermopower wave device (supported by a glass slide) with a thermoelectric harvester placed atop. b) A sample experimental voltage output from an experimental setup as in section a. As can be seen from the plot, the thermal mass of the TE harvester retains heat and continues to give a voltage output even beyond the reaction is completed or stopped. c) Plot of the efficiency of thermopower wave devices versus the fuel content that contributed to the reaction wave. Log values were plotted to be able to accommodate the order of magnitude increase in the efficiency of operation, with using high efficiency fuels and TE harvesters. Efficiency values as high as 1% were demonstrated for sodium azide reaction waves combined with TE harvesting.

Superadiabaticity in 1D and 2D Systems

There have been previous studies investigating steady-state self-propagating reaction waves. In this, we studied various mathematical systems which physically correspond to self-propagating waves, but to the limit of the reaction wave reaching the adiabatic boundary. Our analysis shows that when such a reaction wave impinges on an adiabatic boundary, it can generate temperatures higher than the predicted adiabatic temperature rise.(8)
For example, consider a system of a 1D self-propagating reaction wave. The non-dimensional heat and mass transfer equations are given by:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \xi^2} + we^{-\frac{1}{u}}$$

$$\frac{dw}{d\tau} = -\beta we^{-\frac{1}{u}}$$

The non-dimensional temperature is denoted by u, the non-dimensional fuel concentration by w, the non-dimensional time by τ and the non-dimensional distance coordinate by ξ. When solving the above system of coupled partial differential using the software COMSOL, we see that for simulations for β=4, the maximum temperature at the boundary goes up to (uβ) ~ 1.26 as against the predicted (uβ) ~ 1.

Bounds for this superadiabatic temperature u_{max} were evaluated by considering another system, that of a self-propagating wave impinging against a batch reactor which cannot lose the heat to the surrounding system. An implicit equation that sets bounds on u_{max} was found to be

$$u_{max} = u_{ana} + \frac{we^{-\frac{1}{u_{max}}}}{\gamma\beta}$$

Similar analysis performed for a self-propagating 2D reaction wave also shows presence of superadiabatic temperature at the boundary. Figure 9 shows snap-shots of a triangular waveguide with the reaction initiated along one side, solved by using the governing 2D non-dimensional heat and mass balance equations. We see superadiabatic temperature at the top vertex at non-dimensional time τ=360.

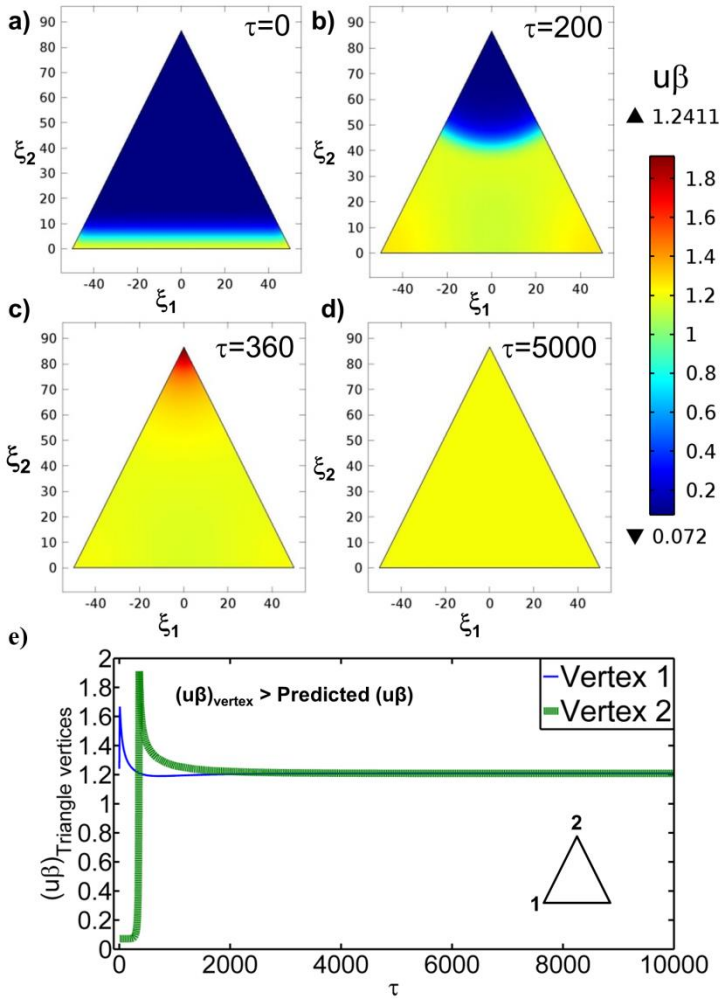

Figure 9: Output from a 2D Cartesian reaction wave simulation for an equilateral triangular geometry with line initiation for β=4. (a-d) Color-maps of temperature at various time points of the simulation. e) This figure shows superadiabatic temperature at the top vertex of the triangle with max temperature as high as 1.9 (From Ref. (8))

Summary: Accomplishments to Date

(** This was used to fill up the abstract in the cover form and SF 298**)

In summary, over the past five years of the grant, we have systematically built the theoretical and experimental underpinnings of a new field in energy research. We experimentally demonstrated the thermopower wave phenomenon, outlining the synthesis and measurement techniques to quantify the energy balance. We also singularly pioneered the theory of these waves, focusing separately on the thermal wave propagation and the resulting concomitant carrier wave generating the electrical power pulse. We have synthesized nitrobenzene functionalized carbon nanotube fibers as thermopower wave generators. We have also theoretically predicted, and experimentally demonstrated, oscillations in voltage from the non-linearity of such waves. We have extended this field to higher efficiency fuels and system configurations. Progress towards energy harvesting from fugitive emissions has been made, with breakthroughs in catalysis and have enabled the extension of thermopower waves to liquid fuels for the first time. The renewal application will allow us to translate this new science and understanding into engineering demonstrations that will impact the fields of energy harvesting and portable power systems.

The Next Directions

(Kept the intro part of the future work part from the older report. Not sure if this part has to be included at all**)**

The next phase of this research will result in two distinct prototype devices as demonstrations, as well as continued development of the soliton wave theory of reaction waves responsible for this effect.
Firstly, we plan to implement an array design for thermopower wave generators with harvesting of any heat not captured by the reaction. Preliminary data shows that this design can boost efficiency by 1000-fold.
Secondly, we plan to use newer solid fuels and combine it with energy harvesting techniques to improve the efficiency of operation of thermopower wave devices.
Thirdly, we continue development of a prototype powered by organic fuel vapor, building upon the results from the previous project period. This Aim involves the solution of a class of variational problems central to the design of this type of pulse powered generator. The novel autocataytic wave propagation scheme, the first of its kind, will result in a prototype capable of sustained power generation over an indefinite number of cycles.
Lastly, we seek to explore the implications of our superadiabaticity theory as Aim 4, experimentally realizing the temperature amplification and designing waveguides to control this effect. We show that the thermal concentration afforded by superadiabaticity may permit it to be transferred by radiation to a visible photovoltaic, generating a novel thermophotovoltaic. Used in conjunction with the thermopower wave itself, this approach may afford even higher efficiencies in fuel conversion.

List of people involved

Prof. Michael S. Strano (Principle Investigator)
Wonjoon Choi (Graduate Student)
Joel T. Abrahamson (Graduate Student)
Sayalee G. Mahajan (Graduate Student)
Anton L. Cottrill (Graduate Student)
Qing Hua Wang (Postdoctoral Associate), etc.

Publications

1. Choi W, Hong S, Abrahamson JT, Han J-H, Song C, Nair N, et al. Chemically driven carbon-nanotube-guided thermopower waves. Nat Mater. [10.1038/nmat2714]. 2010;9(5):423-9.
2. Choi W, Abrahamson JT, Strano JM, Strano MS. Carbon nanotube-guided thermopower waves. Materials Today. 2010;13(10):22-33.
3. Abrahamson JT, Choi W, Schonenbach NS, Park J, Han J-H, Walsh MP, et al. Wavefront Velocity Oscillations of Carbon-Nanotube-Guided Thermopower Waves: Nanoscale Alternating Current Sources. ACS Nano. 2010 2011/01/25;5(1):367-75.
4. Abrahamson JT, Strano MS. Analytical Solution to Coupled Chemical Reaction and Thermally Diffusing Systems: Applicability to Self-Propagating Thermopower Waves. The Journal of Physical Chemistry Letters. 2010 2010/12/16;1(24):3514-9.
5. Abrahamson JT, Song C, Hu JH, Forman JM, Mahajan SG, Nair N, et al. Synthesis and Energy Release of Nitrobenzene-Functionalized Single-Walled Carbon Nanotubes. Chemistry of Materials. 2011 2011/10/25;23(20):4557-62.

6. Abrahamson JT, Sempere B, Walsh MP, Forman JM, Şen F, Şen S, et al. Excess Thermopower and the Theory of Thermopower Waves. ACS Nano. 2013.
7. Mahajan SG, Wang QH, Strano MS, Abrahamson JT. Energy generation using thermopower waves: Experimental and analytical progress. AIChE Journal. 2013;59(9):3333-41.
8. Mahajan SG, Abrahamson JT, Birkhimer S, Friedman E, Wang QH, Beck M, et al. Superadiabaticity in Reaction Waves as a Mechanism for Energy Concentration. Energy & Environmental Science. 2014. 7(10), 3391-3402.

1.

1. Report Type

Final Report

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Grant/Contract Number

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FA9550-09-1-0700

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Michael S. Strano

Program Manager

The AFOSR Program Manager currently assigned to the award

Byung L. (“Les”) Lee

Reporting Period Start Date

09/30/2009

Reporting Period End Date

12/30/2014

Abstract

During the performance period of this grant, we have systematically built the theoretical and experimental underpinnings of thermopower waves as an energy conversion and generation phenomenon. The project systematically explored the thermopower wave phenomenon, outlining the synthesis and measurement techniques to rigorously quantify the energy balance. We also singularly pioneered the theory of these waves, focusing separately on the thermal wave propagation and the resulting concomitant carrier wave generating the electrical power pulse. The Theory of Excess Thermopower allows one to estimate the thermal and electrochemical contributions to power generation for the first time. We also synthesized nitrobenzene functionalized carbon nanotube fibers as thermopower wave generators. We have also theoretically predicted, and experimentally demonstrated, oscillations in voltage from the non-linearity of such waves. We have extended this technology to higher efficiency fuels and system configurations, reaching an unprecedented 3% conversion efficiency as an increase of over 1000 since the project start. Significant progress towards continuous energy harvesting from fugitive emissions has been made, with breakthroughs in catalysis and reactor design extending

thermopower waves to liquid fuels for the first time.

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Archival Publications (published) during reporting period:

1. Choi W, Hong S, Abrahamson JT, Han J-H, Song C, Nair N, et al. Chemically driven carbon-nanotube-guided thermopower waves. Nat Mater. [10.1038/nmat2714]. 2010;9(5):423-9.
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Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

Extensions granted or milestones slipped, if any:

None

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

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Appendix Documents

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